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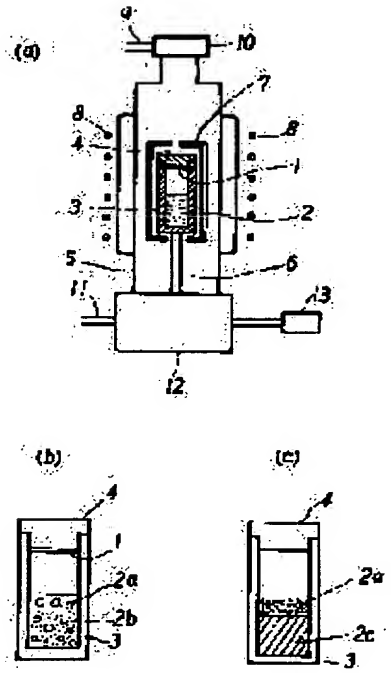
(54) PRODUCTION OF SIC SINGLE CRYSTAL

(57)Abstract:
PURPOSE: To grow SiC single crystal superior in a crystalline property by using high purity Si and C as the raw materials, in the growth of the SiC single crystal using a sublimating recrystallization method.
CONSTITUTION: When the SiC single crystal is grown by a sublimating recrystallization method using starting crystal, Si 2a and C powder 2b or porous graphite 2c are used as the raw materials and the Si 2a and C powder 2b or the porous graphite 2c are reacted to produce the SiC 2, and the SiC is sublimated and the SiC single crystal is grown on the starting crystal 1. Thus, an impurity from the raw materials is prevented and the crystalline property of the SiC single crystal, uniformity and reproducibility are enhanced.



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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the silicon carbide single crystal characterized by including the process which silicon and carbon are made to react and forms silicon carbide, and the process which sublimates the above-mentioned silicon carbide and forms a silicon carbide single crystal on seed crystal.
[Claim 2] The manufacture approach of the silicon carbide single crystal according to claim 1 characterized by for the temperature of the process which forms the above-mentioned silicon carbide being 1150 degrees C or more 1800 degrees C or less, and a pressure being 200 or more Torrs.
[Claim 3] The manufacture approach of a silicon carbide single crystal according to claim 1 that bulk specific gravity is characterized by 1.0 or less graphite block or particle size using carbon powder 10 micrometers or less as the above-mentioned carbon.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of growing up the hexagonal silicon carbide single crystal which used the sublimation recrystallizing method.
[0002]
[Description of the Prior Art] Silicon carbide (SiC) is a semiconductor material which has large forbidden-band width of face (2.2-3.3eV). Moreover, silicon carbide is very stable thermally, chemically, and mechanically, and has the outstanding description that it is strong also to radiation damage. On the other hand, the component using a conventional semiconductor material like silicon is especially difficult to use it under severe conditions, such as an elevated temperature, a high power drive, and radiation irradiation. Therefore, application in a field with the semiconductor device extensive as a semiconductor device which can be used also under such severe conditions using silicon carbide is expected.
[0003] However, the crystal growth technique which can supply the silicon carbide single crystal of the high quality which has a large area to stability on a scale of industrial is not yet established. So, the utilization is obstructed although silicon carbide is a semiconductor material which has the advantage and possibility of above many.
[0004] Conventionally, on a scale of laboratory extent, the silicon carbide single crystal was grown up by the sublimation recrystallizing method (Rayleigh law) for using silicon carbide powder, for example, and the silicon carbide single crystal of the size which can produce a semiconductor device had been obtained. However, the area of the single crystal obtained by this approach is small, and it is difficult to control that dimension and configuration with high precision. Moreover, control of the crystal polymorphism which silicon carbide has, and impurity carrier concentration is not easy, either.
[0005] Moreover, the cubic silicon carbide crystal is grown up by carrying out heteroepitaxial growth on different-species substrates, such as silicon, using chemical vapor deposition (CVD method). Although the single crystal of a large area is obtained by this approach, it is not easy only for the silicon carbide single crystal which includes many defects by a certain thing etc. (-107-/cm2) to be able to grow, but for grid mismatching with a substrate to obtain the silicon carbide single crystal of high quality about 20%.
[0006] advanced Rayleigh who uses silicon carbide powder and seed crystal and performs the sublimation recrystallizing method in order to **** these troubles -- law is proposed (Yu.M.Tairov.andV.F.Tsverkov.J.Crystal Growth, 52 (1981), pp.146-150). If this approach is used, a silicon carbide single crystal can be grown up controlling a crystal polymorphism and a configuration.
[0007]
[Problem(s) to be Solved by the Invention] by the way, conventional advanced Rayleigh -- as the silicon carbide powder used for law -- as the object for abrasives -- ACHIESON -- although the powder manufactured by law is used -- ACHIESON -- the powder manufactured by law contains many impurities, such as aluminum, titanium, and vanadium. Moreover, it is large-sized and it necessary to grind for use as a raw material, and an indeterminate mold and since the degree of

hardness of silicon carbide is large, as for the silicon carbide manufactured by the ACHIESON method, impurity mixing from a grinding fixture also becomes a problem.
[0008] The place which this invention solves the above-mentioned conventional trouble, and is made into the purpose is to offer the manufacture approach of a silicon carbide single crystal that a good silicon carbide single crystal can be manufactured with sufficient repeatability.
[0009]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is based on the manufacture approach of the silicon carbide single crystal characterized by including the process which silicon and carbon are made to react and forms silicon carbide, and the process which sublimates the above-mentioned silicon carbide and forms a silicon carbide single crystal on seed crystal.
[0010] Moreover, this invention is an approach characterized by for the temperature of the process which forms the above-mentioned silicon carbide being 1150 degrees C or more 1800 degrees C or less, and a pressure being 200 or more Torrs.
[0011] Moreover, this invention is the approach that bulk specific gravity is characterized by 1.0 or less graphite block or particle size using carbon powder 10 micrometers or less, as the above-mentioned carbon.
[0012]
[Function] By according to this invention, using the silicon and carbon with an available raw material of a high grade as a start raw material, making silicon and carbon react, forming silicon carbide, sublimating this silicon carbide, and growing up silicon carbide on seed crystal, the defect resulting from an impurity is prevented and the good silicon carbide single crystal excellent in crystallinity can be grown up with sufficient repeatability.
[0013]
[Example] Hereafter, the manufacture approach of the silicon carbide single crystal of this invention is explained to a detail based on an example.
[0014] drawing 1 (a) is drawing showing cross-section structure of manufacturing installation of silicon carbide single crystal concerning example of this invention, and using seed crystal advanced type [equipment / this] Rayleigh -- a silicon carbide single crystal can be grown up by law.
[0015] Drawing 1 (b) is drawing showing the cross-section structure of the crucible at the time of manufacture initiation of the silicon carbide single crystal concerning the example of this invention, and drawing 1 (c) is drawing showing the cross-section structure of the crucible at the time of manufacture initiation of the silicon carbide concerning other examples. The silicon carbide which, as for 1, the silicon carbide single crystal substrate reacted, and, as for 2, silicon and carbon reacted here, and was formed, 2a -- silicon and 2b -- carbon powder and 2c -- a carbon block and 3 -- the crucible made from a graphite, and 4 -- in the crucible lid made from a graphite, the bearing bar of the product [5 / 6 / a duplex quartz tube and] made from a graphite, and 7, a branch pipe, and 10 and 12 show the chamber made from stainless steel, and, as for FERUTO made from a graphite, and 8, 13 shows the vacuum pump, as for a work-piece coil, and 9 and 11.
[0016] Although crystal growth is performed using the manufacturing installation of drawing 1 (a), on the silicon carbide single crystal substrate 1 used as seed crystal, crystal growth makes the silicon and carbon which are a raw material react, forms silicon carbide 2, and is performed by carrying out sublimation recrystallization of the silicon carbide 2. The silicon carbide single crystal substrate 1 of seed crystal is attached in the inside of the crucible lid 4 made from a graphite. As shown in drawing 1 (b) or drawing 1 (c), the interior of the crucible 3 made from a graphite is filled up with the silicon and carbon of a raw material. Such crucible 3 made from a graphite is installed in the interior of the duplex quartz tube 5 by the bearing bar 6 made from a graphite. FERUTO 7 made from a graphite for a heat-shield is installed in the perimeter of the crucible 3 made from a graphite. Moreover, the work-piece coil 8 is wound around the periphery of a duplex quartz tube, by passing the high frequency current to each, the crucible 3 made from a graphite can be heated and a raw material and seed crystal can be heated to desired temperature, respectively. The chamber 10 made from stainless steel equipped with the branch

pipe 9 used as the input of gas is formed in the upper limit of the duplex quartz tube 5. The branch pipe 11 and vacuum pump 13 used as the exhaust port of gas are connected to the chamber 12 made from stainless steel, and the interior of the duplex quartz tube 5 can be exhausted to a desired degree of vacuum.

[0017] Next, manufacture of the silicon carbide single crystal using such crystal growth equipment is explained concretely.

[0018] The 1st example is explained based on drawing 1 (a) and drawing 1 (b).

[0019] First, the substrate 1 with which growth side bearing consists of a silicon carbide single crystal of the hexagonal mold which is a direction (0001) as seed crystal was prepared. And this substrate 1 was attached in the inside of the crucible lid 4 made from a graphite. Moreover, the interior of the crucible 3 made from a graphite was filled up with silicon 2a of a high grade, and carbon powder 2b as a raw material. As silicon 2a, it was granular and grain size used [purity] that whose purity is 4Ns by 10 micrometers as carbon powder 2b of no less than 5 Ns according to the letter of 2-5mm crushing. Subsequently, the crucible 3 made from a graphite filled up with the raw material was closed with the crucible lid 4 made from a graphite furnished with seed crystal, and was installed in the interior of the duplex quartz tube 5 by the bearing bar 6 of a graphite. It covered with FERUTO 7 made from a graphite around the crucible 3 made from a graphite. And argon gas (Ar) was passed inside the duplex quartz tube 5 from the branch pipe 9 of the chamber 10 made from stainless steel as a controlled atmosphere. The flow rate of Ar gas was set as a part for 1l./. Next, it was made for the temperature gradient of silicon 2a, the raw material of carbon powder 2b, and seed crystal 1 to be lost because the temperature of silicon 2a and carbon powder 2b adjusts the location of crucible as 1700 degrees C and a work-piece coil by adjusting a sink and the high frequency current for the high frequency current in the work-piece coil 8. Silicon and carbon react by holding in this condition for 2 hours, and silicon carbide 2 is formed. Then, the high frequency current is adjusted, the location of 2150 degrees C, a work-piece coil, and crucible is adjusted for the temperature of seed crystal, and the temperature of silicon carbide 2 is set as 2200 degrees C. Next, the interior of the duplex quartz tube 5 was decompressed using the vacuum pump 13. It carried out gradually, having applied [this] it for 20 minutes from atmospheric pressure to -30Torr, and it was held with the degree of vacuum of 30Torr. By holding in this condition for 5 hours, the silicon carbide single crystal with a thickness of about 5mm grew.

[0020] Thus, when the obtained silicon carbide single crystal was analyzed by the X-ray diffraction method and Raman spectroscopy, it turned out that the hexagonal silicon carbide single crystal is growing. The grown-up crystal is more uniform than a seed crystal top to a growth maximum front face, and there are also few defects (102cm-2 following) and it is 6H form silicon carbide single crystal of high quality.

[0021] Although the shape of a 2-5mm grain was used by this example as a silicon raw material to be used, the object of other particle size may be used. However, if particle size is not much small, the amount with which it is filled up in crucible will decrease, and the grown-up silicon carbide single crystal becomes small. Moreover, it is 10 micrometers although the 10-micrometer object was used as carbon powder. If the above carbon powder is used, only the front face of carbon powder reacts with silicon, and enough silicon carbide raw materials cannot be formed. Moreover, the silicon carbide single crystal which the amount with which it is filled up in crucible decreased when the particle size of carbon powder was extremely small, and grew becomes small and is not practical.

[0022] Although the conditions of 1700 degrees C and atmospheric pressure were used for making silicon and carbon react in this example, the conditions of 1150-1800 degrees C and atmospheric pressure are used. Below 1150 degrees C, it does not happen, but sublimation of the silicon carbide which 1800 degrees C or more or a pressure reacted on the conditions of 200 or less Torrs, and formed takes place to coincidence, and silicon and a carbon Mr. reaction cannot perform control of a crystal polymorphism.

[0023] Moreover, if the silicon carbide powder formed by the ACHIESON method as a raw material is used, a defect will increase with an impurity (104cm-2 above), and crystallinity will also worsen. Moreover, a transparency property also worsens by absorption by the impurity, and

the good silicon carbide single crystal for substrates cannot be grown up.
[0024] Next, the 2nd example is explained based on drawing 1 (a) and drawing 1 (c). First, it was filled up with silicon 2a of a high grade and graphite block 2c used as a raw material. As silicon 2a, bulk density used [JIS grain size] the porosity graphite of 0.5 as #300 and graphite block 2c. The crucible 3 made from a graphite filled up with these raw materials was closed with the crucible lid 4 made from a graphite which has not attached seed crystal, and was installed in the interior of the duplex quartz tube 5 by the bearing bar 6 made from a graphite. It covered with FERUTO 7 made from a graphite around the crucible 3 made from a graphite. And Ar gas was passed inside the duplex quartz tube 5 from the branch pipe 9 of the chamber 10 made from stainless steel as a controlled atmosphere. The flow rate of Ar gas was set as a part for 1l./. Moreover, it adjusted so that the temperature of sink silicon carbide powder might become 1800 degrees C in the work-piece coil 8 about the high frequency current, and it held for 360 minutes. Silicon and a porosity graphite react by this processing, and silicon carbide 2 is formed. Then, the substrate 1 with which growth side bearing consists of a 4H mold silicon carbide single crystal of the hexagonal mold which is a direction (0001) as seed crystal was prepared. And this substrate 1 was attached in the inside of the crucible lid 4 made from a graphite.
[0025] Next, the crucible 3 made from a graphite filled up with the raw material was closed with the crucible lid 4 made from a graphite furnished with seed crystal, and was installed in the interior of the duplex quartz tube 5 by the bearing bar 6 made from a graphite. It covered with FERUTO 7 made from a graphite around the crucible 3 made from a graphite. And the nitrogen gas for argon gas (Ar) n mold impurity addition (M2) was passed inside the duplex quartz tube 5 from the branch pipe 9 of the chamber 10 made from stainless steel as a controlled atmosphere. The flow rate of Ar gas and N2 gas was set as a part for part 0.8 cc/for 1l./, respectively. Moreover, it adjusted so that the temperature of the sink substrate 1 might become the work-piece coil 8 and the temperature of 2200 degrees C and silicon carbide 2 (b) might become 2300 degrees C about the high frequency current. Then, while adjusting the flow rate of Ar gas, the interior of the duplex quartz tube 5 was decompressed using the vacuum pump 13. It carried out gradually, having applied [this] it for 60 minutes from atmospheric pressure to 10Torr(s), and it was held with the degree of vacuum of 10Torr for 6 hours. By holding in this condition for 8 hours, the silicon carbide single crystal with a thickness of about 8mm grew.
[0026] Thus, it is an X-ray diffraction method about the obtained silicon carbide single crystal. When analyzed by Raman spectroscopy, it turned out that 4H mold silicon carbide single crystal of the hexagonal mold whose growth side bearing is a direction (0001) is growing. A growth rate is n mold silicon carbide single crystal whose resistivity it is 1.0mm/o'clock and is 0.1-ohmcm. A transparency property is also good and homogeneous and a defect is also the n mold 4H form silicon carbide single crystal of high quality few (2 or less [102cm -]).
[0027] Although bulk density used the object of 0.5 as a porosity graphite in this example, bulk density has little silicon 1.0 or more, and growth of a subsequent silicon carbide single crystal cannot do the silicon carbide with which it did not enter into the porosity graphite, but the reaction was formed only on the front face.
[0028] In addition, this invention is not limited to the above-mentioned example, but various modification is possible for it within a claim.
[0029]
[Effect of the Invention] As explained to the detail above, according to this invention, the crystalline and homogeneous outstanding good silicon carbide single crystal can be grown up with sufficient repeatability. Moreover, if a silicon carbide single crystal is grown up on this substrate by the vapor-phase-epitaxial-growth method, using the silicon carbide single crystal obtained by this invention as a substrate for growth, optical and the silicon carbide single crystal excellent in electrical characteristics will be obtained. Therefore, the silicon carbide semi-conductor substrate equipments (for example, a field-effect transistor (FET), a phase amendment metal-oxide-semiconductor integrated circuit (C-MOS), various power components, etc.) excellent in the blue light emitting device excellent in the optical property and electrical characteristics can be manufactured. And since the above-mentioned silicon carbide single crystal can be obtained with sufficient repeatability, optical and the various above-mentioned

silicon carbide semiconductor devices excellent in electrical characteristics are producible with the sufficient yield on a scale of industrial.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] (a) It is drawing showing the cross-section structure of the manufacturing installation of the silicon carbide single crystal concerning the example of this invention.
(b) It is drawing showing the cross-section structure of the crucible at the time of manufacture initiation of the silicon carbide single crystal concerning the example of this invention.
(c) It is drawing showing the cross-section structure of the crucible at the time of manufacture initiation of the silicon carbide single crystal concerning other examples of this invention.
[Description of Notations]
1 Silicon Carbide Single Crystal Substrate (Seed Crystal)
2 Silicon Carbide
2a Silicon
2b Carbon powder
2c Carbon block
3 Crucible made from Graphite
4 Crucible Lid made from Graphite
5 Duplex Quartz Tube
6 Bearing Bar
7 FERUTO made from Graphite
8 Work-Piece Coil
9 11 Between branches
10 12 Chamber made from stainless steel
13 Vacuum Pump

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審査請求　未請求　請求項の数３　ＯＬ　（全　５　頁）

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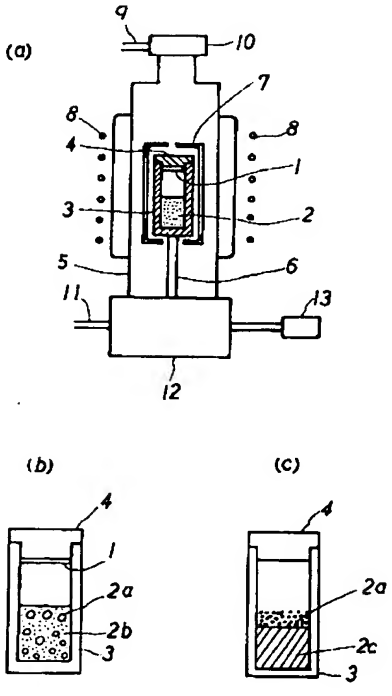
(54)【発明の名称】　炭化珪素単結晶の製造方法

(57)【要約】

【目的】　昇華再結晶法を用いた炭化珪素単結晶成長において、高純度の珪素と炭素を原料として用いることにより結晶性に優れた炭化珪素単結晶を成長する。

【構成】　種結晶を用いた昇華再結晶法により炭化珪素単結晶を成長する際に、原料として珪素２ａおよび炭素粉末２ｂまたは多孔質黒鉛２ｃを用い、珪素２ａおよび炭素粉末２ｂまたは多孔質黒鉛２ｃを反応させて炭化珪素２を形成し、この炭化珪素を昇華させて種結晶１上に炭化珪素単結晶を成長させる。

【効果】　原料よりの不純物を防止し、炭化珪素単結晶の結晶性および均質性、および再現性が向上する。



【特許請求の範囲】
【請求項１】　珪素と炭素を反応させて炭化珪素を形成する工程と、
上記炭化珪素を昇華して種結晶上に炭化珪素単結晶を形成する工程とを含むことを特徴とする炭化珪素単結晶の製造方法。
【請求項２】　上記炭化珪素を形成する工程の温度が１１５０℃以上１８００℃以下で、かつ、圧力が２００Ｔｏｒｒ以上であることを特徴とする請求項１に記載の炭化珪素単結晶の製造方法。
【請求項３】　上記炭素としてかさ比重が１．０以下の黒鉛ブロックまたは粒径が１０μｍ以下の炭素粉末を用いることを特徴とする請求項１に記載の炭化珪素単結晶の製造方法。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は昇華再結晶法を用いた六方晶の炭化珪素単結晶を成長させる方法に関する。
【０００２】
【従来の技術】炭化珪素（ＳｉＣ）は広い禁制帯幅（２．２～３．３ｅＶ）を有する半導体材料である。また、炭化珪素は熱的，化学的、及び機械的に極めて安定であり、放射線損傷にも強いという優れた特徴をもっている。他方、珪素のような従来の半導体材料を用いた素子は、特に高温、高出力駆動、放射線照射などの苛酷な条件下では使用が困難である。したがって、炭化珪素を用いた半導体素子は、このような苛酷な条件下でも使用し得る半導体素子として広範な分野での応用が期待されている。
【０００３】しかしながら大面積を有する高品質の炭化珪素単結晶を、工業的規模で安定に供給し得る結晶成長技術は、いまだ確立されていない。それゆえ、炭化珪素は、上述のような多くの利点及び可能性を有する半導体材料であるにもかかわらず、その実用化が阻まれている。
【０００４】従来、研究室程度の規模では、例えば炭化珪素粉末を用いる昇華再結晶法（レーリー法）で炭化珪素単結晶を成長させ、半導体素子の作製可能なサイズの炭化珪素単結晶を得ていた。しかしながら、この方法では、得られた単結晶の面積が小さく、その寸法及び形状を高精度に制御することが困難である。また、炭化珪素が有する結晶多形及び不純物キャリヤ濃度の制御も容易でない。
【０００５】また、化学的気相成長法（ＣＶＤ法）を用いて珪素等の異種基板上にヘテロエピタキシャル成長させることにより立方晶の炭化珪素結晶を成長させている。この方法では、大面積の単結晶は得られるが、基板との格子不整合が約２０％もあること等により多くの欠陥を含む（～10^7／cm^2）炭化珪素単結晶しか成長できず、高品質の炭化珪素単結晶を得ることは容易でない。
【０００６】これらの問題点を隗血するために、炭化珪素粉末と種結晶を用いて昇華再結晶法を行う改良型レーリー法が提案されている（Ｙｕ．Ｍ．Ｔａｉｒｏｖ．ａｎｄＶ．Ｆ．Ｔｓｖｅｒｋｏｖ．Ｊ．Ｃｒｙｓｔａｌ Ｇｒｏｗｔｈ，５２（１９８１），ｐｐ．１４６－１５０）。この方法を用いれば、結晶多形及び形状を制御しながら、炭化珪素単結晶を成長させることができる。
【０００７】
【発明が解決しようとする課題】ところで、従来の改良型レーリー法に用いる炭化珪素粉末としては、研磨材用としてアチェソン法により製造された粉末を用いているが、アチェソン法により製造された粉末はアルミニウム，チタン，バナジウム等の多くの不純物を含んでいる。また、アチェソン法により製造された炭化珪素は不定型、大型であり、原料としての使用には粉砕する必要があり、炭化珪素は硬度が大きいため粉砕治具からの不純物混入も問題になる。
【０００８】本発明は上記従来の問題点を解決するものであり、その目的とするところは、良質の炭化珪素単結晶を、再現性よく製造し得る炭化珪素単結晶の製造方法を提供することにある。
【０００９】
【課題を解決するための手段】上記目的を達成するため、本発明は、珪素と炭素を反応させて炭化珪素を形成する工程と、上記炭化珪素を昇華して種結晶上に炭化珪素単結晶を形成する工程とを含むことを特徴とする炭化珪素単結晶の製造方法によるものである。
【００１０】また、本発明は、上記炭化珪素を形成する工程の温度が１１５０℃以上１８００℃以下で、かつ圧力が２００Ｔｏｒｒ以上であることを特徴とする方法である。
【００１１】また、本発明は、上記炭素としてかさ比重が１．０以下の黒鉛ブロックまたは粒径が１０μｍ以下の炭素粉末を用いることを特徴とする方法である。
【００１２】
【作用】本発明によれば、高純度の原料が入手可能な珪素と炭素を出発原料とし、珪素と炭素を反応させて炭化珪素を形成し、該炭化珪素を昇華し種結晶上に炭化珪素を成長させることにより、不純物に起因する欠陥を防止し、結晶性に優れた良質の炭化珪素単結晶を再現性良く成長できる。
【００１３】
【実施例】以下、本発明の炭化珪素単結晶の製造方法について実施例に基づき詳細に説明する。
【００１４】図１（ａ）は、本発明の実施例に係る炭化珪素単結晶の製造装置の断面構造を示す図であり、本装置により種結晶を用いた改良型レーリー法により炭化珪素単結晶を成長させることができる。
【００１５】図１（ｂ）は、本発明の実施例に係る炭化

珪素単結晶の製造開始時の坩堝の断面構造を示す図であり、図１（ｃ）は、他の実施例に係る炭化珪素の製造開始時の坩堝の断面構造を示す図である。ここで、１は炭化珪素単結晶基板、２は珪素と炭素が反応して形成された炭化珪素、２ａは珪素、２ｂは炭素粉末、２ｃは炭素ブロック、３は黒鉛製坩堝、４は黒鉛製坩堝蓋、５は二重石英管、６は黒鉛製の支持棒、７は黒鉛製フェールト、８はワークコイル、９と１１は枝管、１０と１２はステンレス製チャンバー、１３は真空ポンプを示している。

【００１６】図１（ａ）の製造装置を用いて結晶成長を行うが、結晶成長は、種結晶として用いた炭化珪素単結晶基板１の上に、原料である珪素と炭素を反応させて炭化珪素２を形成し、炭化珪素２を昇華再結晶させることにより行われる。種結晶の炭化珪素単結晶基板１は、黒鉛製坩堝蓋４の内面に取り付けられる。図１（ｂ）または図１（ｃ）に示すように原料の珪素と炭素は黒鉛製坩堝３の内部に充填されている。このような黒鉛製坩堝３は、二重石英管５の内部に、黒鉛製の支持棒６により設置される。黒鉛製坩堝３の周囲には、熱シールドのための黒鉛製フェールト７が設置されている。また、二重石英管の外周にはワークコイル８が巻回されており、それぞれに高周波電流を流すことにより黒鉛製坩堝３を加熱し、原料及び種結晶をそれぞれ所望の温度に加熱することができる。二重石英管５の上端には、ガスの流入口となる枝管９を備えたステンレス製チャンバー１０が設けられている。ステンレス製チャンバー１２には、ガスの排出口となる枝管１１と真空ポンプ１３が接続されており、二重石英管５の内部を所望の真空度に排気することができる。

【００１７】次に、このような結晶成長装置を用いた炭化珪素単結晶の製造について具体的に説明する。

【００１８】図１（ａ）及び図１（ｂ）に基づき第１の実施例について説明する。

【００１９】まず、種結晶として、成長面方位が（０００１）方向である六方晶型の炭化珪素単結晶からなる基板１を用意した。そして、この基板１を黒鉛製坩堝蓋４の内面に取り付けた。また、黒鉛製坩堝３の内部には、原料として高純度の珪素２ａ及び炭素粉末２ｂを充填した。珪素２ａとしては、粒状で２～５mm破砕状で純度が５Ｎもの、炭素粉末２ｂとしては粒度が１０μｍで純度が４Ｎのものを用いた。次いで、原料を充填した黒鉛製坩堝３を、種結晶を取り付けた黒鉛製坩堝蓋４で閉じ、黒鉛の支持棒６により二重石英管５の内部に設置した。黒鉛製坩堝３の周囲には黒鉛製フェールト７で被覆した。そして、雰囲気ガスとしてアルゴンガス（Ａｒ）を、ステンレス製チャンバー１０の枝管９から二重石英管５の内部に流した。Ａｒガスの流量は１ｌ／分に設定した。次に、ワークコイル８に高周波電流を流し、高周波電流を調節することで珪素２ａと炭素粉末２ｂの温度が１７００℃、ワークコイルとして坩堝の位置を調節することで珪素２ａと炭素粉末２ｂの原料と種結晶１との温度差が無くなるようにした。この状態で２時間保持することで珪素と炭素が反応して炭化珪素２が形成される。続いて、高周波電流を調節して種結晶の温度を２１５０℃、ワークコイルと坩堝の位置を調節し炭化珪素２の温度を２２００℃に設定する。次に、真空ポンプ１３を用いて二重石英管５の内部を減圧した。この減圧は大気圧から～３０Ｔｏｒｒまで２０分間かけて徐々に行い、３０Ｔｏｒｒの真空度で保持した。この状態で５時間保持することにより、約５mmの厚さの炭化珪素単結晶が成長した。

【００２０】このようにして得られた炭化珪素単結晶をＸ線回折法、ラマン分光法により分析したところ、六方晶の炭化珪素単結晶が成長していることがわかった。成長した結晶は種結晶上より成長最表面まで均一で欠陥も少なく（$10^2 cm^{-2}$ 以下）、高品質の６Ｈ形炭化珪素単結晶である。

【００２１】使用する珪素原料として本実施例では２～５mmの粒状を用いたが、他の粒径の物を用いてもよい。しかし、あまり粒径が小さいと坩堝内に充填する量が少なくなり、成長した炭化珪素単結晶が小さくなる。また、炭素粉末として１０μｍの物を用いたが、１０μｍ 以上の炭素粉末を用いると炭素粉末の表面のみが珪素と反応し十分な炭化珪素原料が形成できない。また、炭素粉末の粒径が極端に小さいと坩堝内に充填する量が少なくなり、成長した炭化珪素単結晶が小さくなり実用的でない。

【００２２】本実施例では珪素と炭素を反応させるのに１７００℃、大気圧の条件を用いたが、１１５０～１８００℃、大気圧の条件が用いられる。１１５０℃以下では珪素と炭素殿反応は起こらず、１８００℃以上又は圧力が２００Ｔｏｒｒ以下の条件では反応して形成した炭化珪素の昇華が同時に起こり結晶多形の制御ができない。

【００２３】また、原料としてアチェソン法により形成した炭化珪素粉末を用いると不純物により欠陥が多くなり（$10^4 cm^{-2}$ 以上）結晶性も悪くなる。また、不純物による吸収により透過特性も悪くなり、基板用の良質な炭化珪素単結晶が成長できない。

【００２４】次に、図１（ａ）及び図１（ｃ）に基づき、第２の実施例について説明する。まず、原料となる高純度の珪素２ａと黒鉛ブロック２ｃを充填した。珪素２ａとしては、ＪＩＳ粒度が＃３００、黒鉛ブロック２ｃとしてはかさ密度が０．５の多孔質黒鉛を用いた。これらの原料を充填した黒鉛製坩堝３を、種結晶を取り付けていない黒鉛製坩堝蓋４で閉じ、黒鉛製の支持棒６により二重石英管５の内部に設置した。黒鉛製坩堝３の周囲には黒鉛製フェールト７で被覆した。そして、雰囲気ガスとしてＡｒガスを、ステンレス製チャンバー１０の

枝管９から二重石英管５の内部に流した。Ａｒガスの流量は１ｌ／分に設定した。また、ワークコイル８に高周波電流を流し炭化珪素粉末の温度が１８００℃になるように調節し、３６０分保持した。この処理により珪素と多孔質黒鉛が反応して炭化珪素２が形成される。その後、種結晶として、成長面方位が（０００１）方向である六方晶型の４Ｈ型炭化珪素単結晶からなる基板１を用意した。そして、この基板１を黒鉛製坩堝蓋４の内面に取り付けた。

【００２５】次に、原料を充填した黒鉛製坩堝３を、種結晶を取り付けた黒鉛製坩堝蓋４で閉じ、黒鉛製の支持棒６により二重石英管５の内部に設置した。黒鉛製坩堝３の周囲には黒鉛製フェールト７で被覆した。そして、雰囲気ガスとしてアルゴンガス（Ａｒ）、ｎ型不純物添加用の窒素ガス（M_2）を、ステンレス製チャンバー１０の枝管９から二重石英管５の内部に流した。Ａｒガス、N^2ガスの流量はそれぞれ１ｌ／分、０．８ｃｃ／分に設定した。また、ワークコイル８に高周波電流を流し基板１の温度が２２００℃、炭化珪素２（ｂ）の温度が２３００℃になるように調節した。続いて、Ａｒガスの流量を調節すると共に、真空ポンプ１３を用いて二重石英管５の内部を減圧した。この減圧は大気圧から１０Ｔｏｒｒまで６０分間かけて徐々に行い、１０Ｔｏｒｒの真空度で６時間保持した。この状態で８時間保持することにより、約８mmの厚さの炭化珪素単結晶が成長した。

【００２６】このようにして得られた炭化珪素単結晶をＸ線回折法、。ラマン分光法により分析したところ、成長面方位が（０００１）方向である六方晶型の４Ｈ型炭化珪素単結晶が成長していることがわかった。成長速度は１．０mm／時であり、抵抗率が０．１Ωｃｍであるｎ型炭化珪素単結晶である。透過特性も良好、均質で欠陥も少なく（$10^2 cm^{-2}$以下）、高品質のｎ型４Ｈ形炭化珪素単結晶である。

【００２７】本実施例では多孔質黒鉛としてかさ密度が０．５の物を用いたが、かさ密度が１．０以上では珪素が多孔質黒鉛の中に入っていかず、反応が表面のみで形成された炭化珪素は少なく、その後の炭化珪素単結晶の成長ができない。

【００２８】なお、本発明は上記実施例に限定されず、請求の範囲内にて種々の変更が可能である。

【００２９】

【発明の効果】以上詳細に説明したように、本発明によれば、結晶性及び均質性の優れた良質の炭化珪素単結晶を再現性よく成長させることができる。また、本発明により得られた炭化珪素単結晶を成長用基板として用い、気相エピタキシャル成長法により、この基板上に炭化珪素単結晶を成長させれば、光学的および電気的特性に優れた炭化珪素単結晶が得られる。したがって、光学的特性に優れた青色発光素子および電気的特性に優れた炭化珪素半導体基板装置（例えば、電界効果トランジスタ（ＦＥＴ），相補正モス集積回路（Ｃ－ＭＯＳ），および各種パワー素子など）を製作することができる。しかも、上記炭化珪素単結晶を再現性よく得られるので、光学的および電気的特性に優れた上記の各種炭化珪素半導体装置を工業的規模で歩留りよく生産することができる。

【図面の簡単な説明】

【図１】（ａ）本発明の実施例に係る炭化珪素単結晶の製造装置の断面構造を示す図である。

（ｂ）本発明の実施例に係る炭化珪素単結晶の製造開始時の坩堝の断面構造を示す図である。

（ｃ）本発明の他の実施例に係る炭化珪素単結晶の製造開始時の坩堝の断面構造を示す図である。

【符号の説明】

１　炭化珪素単結晶基板（種結晶）
２　炭化珪素
２ａ　珪素
２ｂ　炭素粉末
２ｃ　炭素ブロック
３　黒鉛製坩堝
４　黒鉛製坩堝蓋
５　二重石英管
６　支持棒
７　黒鉛製フェールト
８　ワークコイル
９．１１　枝間
１０．１２　ステンレス製チャンバー
１３　真空ポンプ

【図１】